Alkylphenols & Ethoxylates Research Council
Comments for Washington Ecology on APEs
December 19, 2019

Attachment II
Summary of Environmental Monitoring for Nonylphenol and Nonylphenol Ethoxylates in the State of Washington

In an effort to better understand the environmental occurrence for 4-nonylphenol (NP), nonylphenol ethoxylates (NPE), octylphenol (OP) and octylphenol ethoxylates (OPE) in the environment in the State of Washington, the Alkylphenols & Ethoxylates Research Council (APERC) sponsored an analysis of available environmental monitoring data in the state.[1, 2] Results are discussed below and presented in Attachment II Figures 1 though 12.

Environmental monitoring data from the State of Washington were queried from publicly available governmental monitoring programs and were compiled into a statewide database. Monitoring programs included the Department of Ecology, State of Washington, Environmental Information Management System (EIM) and the National Water Quality Monitoring Council (NWQMC), Water Quality Portal (WQP). The EIM contains environmental monitoring data collected by Department of Ecology scientists and their partners, including the Department of Natural Resources and Parks, the University of Washington, the US Army Corps of Engineers, and consultants of the Department of Ecology. The WQP is a cooperative service sponsored by the NWQMC, the Environmental Protection Agency (EPA), and United States Geological Survey (USGS). Nationwide, the WQP serves data collected by over 400 state, federal, tribal, and local agencies. A literature search was also conducted that identified one additional environmental monitoring data resource in the State of Washington by Meador, J.P. et al, 2016, which was included in the database.[3]

The environmental monitoring database contains historical and current data generated by multiple sources using a variety of standards and quality assurance programs. Historical data are generally less robust in study detail than current data. The NWQMC addressed this matter in 2006 with the publication of *Data Elements for Reporting Water Quality Monitoring Results for Chemical, Biological, Toxicological, and Microbiological Analytes*.[4] With that report, the

[1] Tazelaar, D. and Stolz, S. (O'Brien & Gere Engineers, Inc, Ramboll Group) (2019, November 25) Summary of NP and TNPEQ Environmental Monitoring Data in the State of Washington Figures 1-8.
[2] Tazelaar, D. and Stolz, S. (O'Brien & Gere Engineers, Inc, Ramboll Group) (2019, December 5) Summary of OP Environmental Monitoring Data in the State of Washington Figures 9-15.
[3] Meador, J. P., Yeh, A., Young, G., & Gallagher, E. P. (2016). Contaminants of emerging concern in a large temperate estuary. *Environmental pollution*, *213*, 254-267.
[4] National Water Quality Monitoring Council(2006, April) Technical Report No. 3 Data Elements for Reporting Water Quality Monitoring Results for Chemical , Biological, Toxicological, and Microbiological Analytes. https://acwi.gov/methods/pubs/wdqe_pubs/wqde_trno3.pdf

NWQMC developed sets of data elements which they believe are the minimum elements necessary to foster the comparability and exchange of data. In spite of the potential variability in data reliability among the available resources, the entire breadth of data queried was considered and included in the environmental database. Highly variable data were assessed on a study-specific basis and clearly delineated in the summaries herein. Marine and freshwater sediment and surface water data were summarized in both maps and tables in the attached Figures 1 through 12. Efforts to omit replicate and duplicate samples were made after identifying records with duplicative sample detail. When sample-specific detail lacked the distinction of either freshwater or marine, the waterbody detail was used derive that information. Data queried and compiled in the environmental database were subjected to internal quality control checks for accuracy of transposition at a frequency of 10%. For undetected sample results, half the reporting limit (RL) was assigned as a proxy value. For samples that had no reported RL, half the method detection limit (MDL) was assigned as the proxy value. Results reported as estimated values (J flags) were treated as detected results.

Presentation of Environmental Monitoring Data

Results are presented in Figures 1 though 12 that represent detected and non-detected results of NP, Total NP Equivalents (TNPEQ) and OP collected in fresh surface water, marine surface water, freshwater sediment, and marine sediment in Washington between 1997 and 2018. Available monitoring data for NP and are presented in Figures 1 through 4. Aggregate TNPEQ concentrations for NP and NP ethoxylates are presented in Figures 5 through 8. TNPEQ concentrations were calculated according to the Toxicity Equivalence Factors (TEF) relative to NP in Table 1 below, which were originally developed by Environment Canada and later corroborated by Coady et al, 2010. [5, 6] Available monitoring data for OP are presented in Figures 9 through 12 and are presented according to the TEF for OP relative to NP, which was also developed by Environment Canada. There were no results for OPE available.

TABLE 1 Toxicity Equivalence Factors for NP, NPEs, OP and OPEs (Environment Canada, National Guidelines and Standards Office, 2001, April)

Compound	TEF
NP	1
NP1,2EO	0.5
NP3-17EO	0.005
OP	1
OP1,2EO	0.5
OP3-17EO	0.005

[5] Environment Canada, National Guidelines and Standards Office (2001, April). Canadian Environmental Quality Guidelines for Nonylphenol and Its Ethoxylates. Scientific Supporting Document

[6] Coady, K., Staples, C. Losey, B., and Klecka, G. (2010). A Hazard Assessment of Aggregate Exposure to Nonylphenol and Nonylphenol Mono- and Di-ethoxylates in the Aquatic Environment. *Human and Ecological Risk Assessment: An International Journal*. Volume 16, Issue 5, pgs 1066-1094

Data are reported in accordance with US EPA Guidance on Environmental Data Verification and Data Validation. [7] Detected results were presented as reported. Tabular results in Figures 1 though 12 present detected samples in the top row. The bottom row of each table presents all samples in the date range including detected and non-detected samples, which are reported as proxy values of ½ RL or ½ MDL. The number of samples (n), average, standard deviation (StDev), and maximum (Max) values are also reported in the tabular results.

Comparison of Environmental Monitoring to Toxicity-Based Water Quality Criteria and Predicted No Effect Concentrations

All results for NP, TNPEQ, and OP including detected values and proxy non-detected values (1/2 RL or MDL) are presented relative to US EPA Water Quality Criteria (WQC) for NP for media where WQC are available, or to toxicity-based Predicted No Effect Concentrations (PNECs) for NP.[8,9,10] US EPA WQC "represent the concentration in water at which aquatic life are protected from acute and chronic adverse effects".[11]

U.S. EPA developed WQC for NP based on a robust aquatic toxicity database for NP that included adverse effects observed in *in vivo* toxicity studies that characterize population level effects in the environment (*i.e*. effects on survival, growth and development, and reproduction) and consideration of acute to chronic ratios. [12,13] NP has been the subject of attention due to its toxicity to aquatic organisms and because some studies have indicated that NP exhibits weakly estrogenic properties. In its final WQC document, EPA noted "the ability of nonylphenol to induce estrogenic effects has seldom been reported at concentrations below the freshwater final chronic value of 6.5965 μg/L."[14]

A review of more recent aquatic toxicity studies (17 freshwater species and 13 marine species) on NP, NP1EO and NP2EO that were available after US EPA developed the WQC for NP was conducted by Coady et al, 2010, which confirmed that these newer data also support that the US EPA chronic WQC for NP in freshwater and saltwater are protective of aquatic species. [15]

---

[7] US EPA (2002, Nov. 20) Guidance on Environmental Data Verification and Data Validation. EPA QA/G-8 https://www.epa.gov/sites/production/files/2015-06/documents/g8-final.pdf

[8] US Environmental Protection Agency (US EPA). (2005). Aquatic life ambient water quality criteria - nonylphenol. Report 822-R-05-005. US Environmental Protection Agency, Washington, DC, USA.

[9] US Environmental Protection Agency (US EPA). (2006, February 23). Notice of availability of final aquatic life ambient water quality criteria for nonylphenol. Federal Register, 71 (36), 9337-9339.

[10] Staples, C.A., Coady, K. and Losey, B. (2010, Nov). Assessing the Effects and Potential Risk of Branched para-Nonylphenol to Sediment Dwelling Organisms. Poster Presentation at Society of Environmental Toxicology and Chemistry, North American Annual Meeting, Portland, OR, USA

[11] US Environmental Protection Agency (US EPA). (2005).

[12] US Environmental Protection Agency (US EPA). (2005).

[13] US Environmental Protection Agency (US EPA). (2006, February 23).

[14] US Environmental Protection Agency (US EPA). (2005).

[15] Coady, K., Staples, C. Losey, B., and Klecka, G. (2010).

U.S. EPA WQC are appropriate from both a regulatory policy and scientific perspective for evaluating whether environmental exposure patterns indicate a significant environmental source or use of a priority chemical under the Safer Products for Washington. Since US EPA has not yet developed sediment WQC, toxicity-based Predicted No Effect Concentrations (PNECs) for benthic organisms based on studies with sediment concentrations of NP and derived according to methods similar to US EPA guidance are used for comparison. [16]

Table 2 presents the WQC and PNECs used is this evaluation of environmental monitoring data for NP, TNPEQ and OP in the State of Washington.

TABLE 2 NP WQCs(aq) and PNEC(sed)

Media	**Type**	**WQC (µg/L)**	**Source**
Water	Freshwater, acute	28.0	US EPA (2005,2006)
	Freshwater, chronic	6.6	US EPA (2005,2006)
	Saltwater, acute	7.0	US EPA (2005,2006)
	Saltwater, chronic	1.7	US EPA (2005,2006)
Media	**Type**	**PNEC (ng/g-dw)**	**Source**
Sediment	Freshwater	6,150	Staples (2010, Nov)
	Marine	1,230	Staples (2010,Nov)

Analytical Methods

Analytical methods were not consistent across the dataset due to the fact that the data are drawn from different monitoring programs. Consequently RLs and MDLs vary in sensitivity, accuracy and precision across the dataset. However, most analytical methods used in this dataset are sufficiently sensitive to allow comparison to WQC and PNEC values.

In one case, monitoring data conducted in the Lummi Nation, a self-governing nation of the third largest tribe in Washington State, reports values for "NP, total" using an analytical method that is not suitable for the detection of NP or NPE. The Lummi Nation data for "NP, total" was collected using National Environmental Methods Index (NEMI) Standard Method No. 5540C "Anionic Surfactants in Water as MBAS". [17] NPE is a ***nonionic*** surfactant. NEMI Standard Method No. 5540C is a method for anionic surfactants and has not been validated for the detection of 4-NP, 4-t-OP and their ethoxylates; therefore is not suitable for use in monitoring these substances. Since the Lummi Nation fresh surface water data for "NP, Total" are questionable, they are presented separately in Figure 1 "NP Sample Results in Fresh Water, Surface Water" and Figure 5 "Total NP Equivalent Sample Results in Freshwater, Surface

[16] Staples, C.A., Coady, K. and Losey, B. (2010, Nov).
[17] National Environmental Methods Index Standard Method No. 5540C "Anionic Surfactants in Water as MBAS" https://www.nemi.gov/methods/method_summary/7612/

Water". The only detected results in the entire dataset for NP that exceeded benchmark WQC and PNECs were from this Lummi Nation dataset.

An equally important issue that should be recognized is uncertainty more generally with the analytical methodology for measuring NP in water samples, which is related to a high occurrence of false positive detection of this compound even with validated analytical methods. The high degree of analytical bias for false positive detections of NP in surface waters indicates that available monitoring data overstate the actual occurrence and concentrations of this compound in the environment. A published paper by Vanderford *et al*, 2014 presented the results of a large-scale interlaboratory comparison study of 25 chemicals of concern (CECs), including NP to assess the accuracy and precision of available analytical methods with spiked samples of drinking water and source water. [18] The paper presents the results of two single-blind interlaboratory comparisons conducted at 25 research and commercial labs located in the EU, the United States, Canada and Australia. The study evaluated 10 different analytical methods for measuring NP in drinking water and 11 different methods for measuring NP in source water. The authors state that NP is difficult to analyze accurately at the low concentrations expected to be found in the environment and 69% of all unspiked samples were reported to have detectable NP, indicating an extremely high percentage of false positives. The rate of false negative results for NP was only 9%, suggesting only a low degree of concern for generating false negative results. The overall results for NP precluded the authors from recommending specific analytical methods for this compound. The authors concluded: "Perhaps most importantly, results from this work likely suggest that some studies in the literature have very high degrees of analytical bias and/or large numbers of false positives. Further, the use of occurrence data from unsuitable analytical procedures may have resulted in inappropriate risk assessments and prioritization for regulation. Thus, it is important that the consequences these data potentially have had on past decisions is recognized and critical that analytical quality and reliability be considered in future assessments." [19]

Discussion of Results

In Figure No. 1 when the questionable samples from the Lummi Nation monitoring program, which were measured with an analytical method that is not suitable or validated for NP/NPE, are removed from the data set none of the detected or proxy non-detected sampling results for NP taken in fresh surface water between 1997 and 2018 exceeded the EPA WQC (freshwater, chronic) of 6.6 µg/L NP.

[18] Vanderford, B.J., Drewes, J.E., Eaton, A., Guo, Y.C., Haghani, A., Hoppe-Jones, C., Schluesener, M.P., Snyder, S.A., Ternes, A. and Wood, C.J. (2014**).** Results of an Interlaboratory Comparison of Analytical Methods for Contaminants of Emerging Concern in Water. *Anal. Chem.*, *86* (1), pp 774–782

[19] Vanderford, B. J., et al. (2014).

In Figure No. 2 none of the detected or proxy non-detected NP results in marine surface water taken between 2006 and 2018 exceeded the US EPA WQC (chronic, marine) of 1.7 μg/L. No sampling results were available before 2006.

In Figure No. 3 none of the detected or proxy non-detected NP results taken in freshwater sediment between 1997 and 2018 exceeded the toxicity-based PNEC (freshwater, sediment) of 6,150 ng/g dw.

In Figure No. 4 none of the detected NP results in marine sediment in samples taken between 1997 and 2018 exceeded the toxicity-based PNEC (marine, sediment) of 1,230 ng/g dw. Proxy values for 2 of 1139 non-detected samples exceeded the PNEC (marine, sediment) due to the fact that ½ the RLs in the analytical method exceeded the PNEC (marine, sediment). The actual measured maximum value in marine sediment was 350 ng/g dw, which is almost four times less than the PNEC.

In Figure No. 5 when the questionable samples from the Lummi Nation monitoring program, which were measured with an analytical method that is not suitable or validated for NP/NPE, are removed from the data set, none of the detected or proxy non-detected sampling results for aggregated TNPEQ samples taken in fresh surface water between 1997 and 2018 exceeded the EPA WQC (freshwater, chronic) of 6.6 μg/L NP.

In Figure No. 6 none of the aggregate detected or proxy non-detected TNPEQ results in marine surface water taken between 2006 and 2018 exceeded the US EPA WQC (chronic, marine) of 1.7 μg/L. No sampling results were available before 2006.

In Figure No. 7 none of the detected or proxy non-detected aggregate TNPEQ results taken in freshwater sediment between 1997 and 2018 exceeded the toxicity-based PNEC (freshwater, sediment) of 6,150 ng/g dw.

In Figure No. 8 none of the detected aggregate TNPEQ results in marine sediment in samples taken between 1997 and 2018 exceeded the toxicity-based PNEC (marine, sediment) of 1,230 ng/g dw. Proxy values for 3 of 1139 non-detected samples exceeded the PNEC (marine, sediment), due to the fact that ½ the RL in an analytical method exceeded the PNEC (marine, sediment). The actual measured aggregate maximum values in marine sediment was 350 ng/g dw, which is almost four times less than the PNEC.

In Figure 9 none of the detected or proxy non-detected OP results in fresh surface water taken between 1997 and 2018 exceeded the EPA WQC (freshwater, chronic) of 6.6 μg/L NP.

In Figure 10 none of the detected or proxy non-detected OP results in marine surface water taken between 2006 and 2018 exceeded the US EPA WQC (chronic, marine) of 1.7 μg/L. No sampling results were available before 2006

In Figure 11 none of the detected or proxy non-detected OP results for freshwater sediment taken between 2006 and 2018 exceeded the exceeded the toxicity-based PNEC (freshwater, sediment) of 6,150 ng/g dw. No sampling results were available before 2006.

In Figure 12 non of the detected or proxy non-detected OP results for marine sediment taken between 2006 and 2018 exceeded the toxicity-based PNEC (marine, sediment) of 1,230 ng/g dw. No sampling results were available before 2006.

In summary, none of the detected NP, TNPEQ, or OP values from validated analytical methods reported for the 21-year period between 1997 and 2018 exceeded EPA WQC for NP in fresh surface water (6.6 μg/L NP) or marine surface water (1.7 μg/L NP). Also, none of the detected values exceeded toxicity based PNECs in freshwater or marine sediment. There were two cases where exceedances of these WQC and PNEC were reported in the dataset. The first was proxy data reported for **non-detected** samples due to the fact that the RL or MDL for the analytical method exceeded the relevant WQC or PNEC. The second source was questionable data reported under a Lummi Nation monitoring program using a method that is not relevant to or validated for NP, or NPEs, which is discussed under the Analytical Methods section above.

It should be noted that the paper by Meador et al, 2006, which was used as a source to for this environmental monitoring dataset, misreported the US EPA WQC (marine) as 1.7 ng/L, which is one thousand fold less than the actual US EPA WQC (marine) of 1.7 μg/L.[20] Therefore, the authors erroneously concluded that the concentrations they reported (14 – 41 ng/L) in estuaries in the State of Washington exceeded the US EPA WQC.

Temporal Comparison of Monitoring Data

Data in Figures 1 through 12 were presented in two time frames (1997-2005 and 2006-2018) to allow comparison of monitoring results before and after a Wal-Mart initiative that began in 2006 to promote reductions in the use of NPEs in consumer laundry and cleaning products.[21] As summarized above, the data indicate that measured concentrations of NP and TNPEQ are well below EPA WQC for fresh and marine surface water and toxicity-based PNECs for freshwater and marine sediment both before and after NPE reduction initiatives, which began in 2006. In addition, non-detects for NP and TNPEQ represent approximately 97% of the samples reported between 1997 and 2018.

Unfortunately, sampling locations were not selected by the monitoring programs for direct temporal comparison and there are an insufficient number of samples with actual measured detections both before and after the cutoff in 2005/2006 to provide a useful temporal comparison. However, the overall data do not suggest any uses or use patterns either before or

[20] Meador, J.P., Yeh, A., Young, G. and Gallagher, E.P.(2016). Contaminants of emerging concern in a large termperate estuary. *Environmental Pollution*, 213, 254-267.
[21] Wal-Mart. Preferred Chemical Principles . October 2006.

after market reductions in the use of NPEs that represent a significant source, exposure or risk to the environment in the State of Washington.

December 17, 2019